

Hydrazine Detection with a Tunable Diode Laser Spectrometer

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ABSTRACT

Several instruments have been developed to measure low concentrations of hydrazine but none are completely satisfactory. A brief review is presented of current instruments such as the electrochemical cell, the ion mobility spectrometer, the mass spectrometer, the gas chromatograph, and the electronic nose.

A lead-salt tunable diode laser cooled to 85 K and operating near 962-966 cm^{-1} was used to record direct absorption and second-derivative spectra of hydrazine at several pressures to study the sensitivity to low levels of hydrazine. Spectra of NH_3 and CO_2 were used for wavelength identification of the scanned region. With a pathlength of 80 m, detection sensitivities of about 1 ppbv were achieved for hydrazine in dry nitrogen at a cell pressure of 100 mbar.

Pure Hydrazine was injected into the multipass sample cell of an existing Laser Infrared Absorption Spectrometer. Dry nitrogen gas was used as a buffer gas to produce sample cell pressures in the range of 5mbar to 1 atm. The instrument is a tunable diode laser spectrometer that uses high-resolution laser absorption in the 3-8 micrometer wavelength region. The instrument samples the atmosphere using a fast flow system. The flow system is in two parts, a heated inlet with wall temperatures of 60-70 C, and a multipass Optical (Herriott) cell. All interior surfaces are coated with a halocarbon wax from a chloroform solution to minimize wall loss.

For spectroscopic detection of Hydrazine, spectral regions including strong ammonia or carbon dioxide lines must be avoided. Strong hydrazine absorption features were identified at 940 cm^{-1} showing minimal contribution from ammonia interferences as suitable candidates for hydrazine gas detection. For the studies reported here, our particular laser diode could only cover the narrow regions near 962 cm^{-1} and 965 cm^{-1} where strong ammonia interferences were expected. However, the high resolution (0.001 cm^{-1}) of the TDL spectrometer allowed individual lines of hydrazine to be identified away from interferences from either ammonia or carbon dioxide, especially at lower pressures. We identified a Hydrazine line at 961.75 cm^{-1} free from ammonia absorption which would be suitable to monitor hydrazine levels. The paper also shows data on the degradation of the detectivity of hydrazine with increasing pressure.

INTRODUCTION

Hydrazine (N_2H_4 or HZ), monomethylhydrazine ($\text{N}_2\text{H}_3\text{-CH}_3$ or MMH), and unsymmetrical dimethylhydrazine ($\text{N}_2\text{C}_2\text{H}_8$ or UDMH) are used as hypergolic fuels in spacecraft by the National Aeronautics and Space Administration (NASA) and the United States Air Force (USAF). These fuels are highly toxic and are suspected carcinogens, which requires adequate ambient air monitoring of personnel working near these fuels.

In 1995 the American Conference of Governmental Industrial Hygienists (ACGIH) lowered the threshold limit value (TLV) for these fuels to 10 parts per billion (ppb). Instruments to measure such low concentrations have been developed, but they are not completely satisfactory. Several requirements such as quick response, online operation, consumable-free operation, stable calibration, interference-free operation, hand-held portability, reasonable cost, etc. are not easy to satisfy.

NASA, at the John F. Kennedy Space Center (KSC), in conjunction with the USAF, has carried out a project at the NASA/KSC Toxic Vapor Detection Laboratory (TVDL) to develop a portable fuel detector that satisfies the requirements. These efforts have resulted in the use of an instrument that uses an electrochemical cell. The instrument does not meet the

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requirements of quick response and low maintenance but it is widely used in the industry. The Safety and Risk Management Division of NASA assigned a task to JPL to review other approaches to Hydrazine detection in order to identify a portable accurate Hydrazine detection system concept that meets the exposure level requirements of the ACGIH of 10 parts per billion. Other requirements were to identify a system that can be "hand held", that is lightweight, and that can be qualified for "space flight environment", as well as for use at launch sites.

REVIEW OF DETECTION SYSTEMS

A survey of new instrument developments was made to identify possible candidates for further work.. This led to a selection of major concepts that could possibly meet the requirements of measuring 10 ppb of Hydrazine. These major concepts are summarized below.

Electrochemical Gas Detector

NASA at Kennedy Space Center contracted with three instrument manufacturers to develop a portable fuel vapor detector capable of quantifying 10-ppb concentrations in real time. The NASA Toxic Vapor Detection Laboratory at KSC designed and assembled a vapor generation system that can reliably provide 1 to 1400 ppb of MMH, HZ, and UDMH vapors under a wide range of relative humidity conditions for testing the prospective detectors.

Tests of candidate systems (Ref. 1) have resulted in the selection of the Electrochemical Gas Detector, as manufactured by Interscan Corporation as the main detector being used at KSC today. Over a 100 portable units have been procured. This unit therefore presents the baseline against which other candidates will be compared.

The Interscan voltammetric sensor is an electrochemical gas detector operating under diffusion controlled conditions. Gas molecules from the sample are adsorbed on an electrocatalytic electrode, after passing through a diffusion medium, and are electrochemically reacted at an appropriate sensing electrode potential. Figure 1 shows a diagrammatic illustration of the Interscan sensor.

The Hydrazine Compact Portable Analyzers have a 0-1000 ppb range, a minimum detectability of 2 ppb and an alarm at 10 ppb, a response time of 2 minutes to 50 % of final value at 10 ppb, and a fall time of 2 minutes to 50 % of final value. The weight is 8 lbs. The main problem here is the slow response time of 2 minutes to 50 % of final value. In practice, the unit also requires frequent maintenance (monthly) to add water to the electrolyte, as it dries out. The main disadvantages are therefore the slow response and monthly maintenance.

Ion Mobility Spectrometer

When a gaseous ion at atmospheric pressure is placed in a constant electric field, it accelerates down the field until it collides with a neutral molecule, accelerates again until it has another collision, and so forth. This chaotic sequence of accelerations and collisions at the molecular level translates into a constant ion velocity over macroscopic distances. The ratio of the ion velocity to the magnitude of the electric field is called the ion mobility, and separation of ions on the mobility differences is called ion mobility spectrometry (IMS). Because it can measure ion currents below 10^{-12} A, IMS is highly sensitive as a detection technique. The combination of moderate separating power with trace-level sensitivity has led to applications as a stand-alone monitor and a chromatographic detector (Ref. 2). Figure 2 shows a schematic of an IMS cell.

In summary, the advantages of IMS are: high sensitivity, instrumental simplicity, low cost, analytical flexibility, and real-time monitoring capability. A new technique for ionization is to add trace dopants to the spectrometer to tailor its response to specific classes of compounds to enhance the sensitivity or selectivity (Ref. 3). Applications for IMS have been in explosives, chemical warfare agents, drugs of abuse, and atmospheric and workplace pollutants.

Graseby Dynamics of England has developed a Chemical Agent Monitor (CAM), for use by soldiers under battlefield conditions. A commercial version of CAM, called the AVM, was produced to investigate the applications for IMS in Industrial Hygiene. A unit was tested at the Toxic Vapor Detection Laboratory at KSC during 1991-1992 (Reference 4) and several problems were encountered, the major ones being the ability to distinguish between MMH and Ammonia, and poor Response/Recovery times. Another unit was flown onboard STS-37 Atlantis in 1991 and underwent pre- and postflight calibrations at KSC. Similar results were obtained (Reference 5). Other companies have entered the field more recently, and commercial applications add up to over 400 IMS analyzers being used in the field today, primarily in the petroleum industry.

Gas Chromatography

Recent work in GC has shown that the minimum level of detection can be down to 1 ppb with a cycle time of less than 30 seconds, provided the unit is designed for such requirements. The selection of the right detector is of primary importance (Ref. 6). A miniaturized GC has been reported in the literature (Ref. 7). This unit had the dimensions of 15 by 25 by 37 cm and contained a cotton inlet scrubber, miniature ambient temperature trap preconcentrators based on carbon molecular sieve adsorbents, a miniaturized fast capillary column GC coupled to a pulsed flame photometric detector (PFPD), with control software for automated data acquisition, chromatographic peak detection and integration. Support hardware includes a 24-bit acquisition board, GC controller board, on-board processing and data logging, with computer control of pump, valves, heater and temperature controls, and trap cooling fan. For a hydrazine application the inlet scrubber and the preconcentrator with trap cooling fan are not needed. It is estimated that a carrier gas flow (say Helium) of 1 ml per minute will be required. Small aluminum gas cylinders of 150 ml at 1500 psi would provide 250 hours of operation. A portable unit weighing 10-15 lbs appears feasible.

The only requirement that cannot be met is instant response, as the cycle time is of the order of 30 seconds. However, this is considerably better than the 2 minutes for 50 % rise of the electrochemical baseline unit. A GC will also make a good facility instrument.

Miniature Mass Spectrometer

JPL is developing a hand-held mass spectrometer tool designed for astronaut use during Extravehicular Activity (EVA), (Ref. 8). The sensitivity is estimated to be 30 ppb for a system weight of 1.5 kg (3.3 lbs). This includes a data processor but not a vacuum pump. For earth applications a vacuum system (down to 10^{-5} torr) is required but the additional weight of a small vacuum pump (2-3 lbs) would be acceptable for a hand-held system. Battery weight also has to be added for an estimated total system weight under 10 lbs. Figure 3 shows an artist's concept of the use of the Trace Gas Analyzer (TGA) by an astronaut. It suggests the small size of the instrument. The quadrupole rods are only 25 mm in length and 2 mm in diameter. A prototype is being constructed for a flight on the Shuttle in 1999.

It is apparent that all requirements can be met with a miniature quadrupole instrument except the minimum sensitivity of 10 ppb. This development needs to be closely followed as there is considerable promise for a light handheld detector with instant response. Another advantage is that a mass spectrometer can detect a variety of chemical compounds.

Conductive Polymer-Based Sensor

Initial work was done with a single sensor of conductive polymer. The sensor consists of a thin film of polymer/dopant that absorbs/reacts with the hydrazine and as a result changes its electrical conductivity. The polymer can have a thickness in the range of 1500 to 6000 angstroms. The polymer is mounted on a substrate of quartz with a 1000 angstrom layer of gold to provide the electrical contacts for resistance measurements. The result is a sensor that looks like a "chip".

The change in resistance after exposure to Hydrazine was irreversible and the sensor can therefore only be used as a dosimeter. The resistance increase was proportional to the dose by a logarithmic function. Tests in 1993 at the NASA TVDL at KSC exhibited a minimum detectable dose in the range of 1 to 2 ppb-hr, i.e. an exposure of one hour to 1 to 2 ppb of hydrazine. The sensor tested had a saturation dose of approximately 150 ppb-hr in humid conditions. The allowed threshold limit value (TLV) is 10 ppb which corresponds to 80 ppb-hr (8 hours at the TLV level of 10 ppb). The use as a personal dosimeter therefore appeared promising (Ref. 9). However in subsequent tests the sensor had trouble handling a sudden large dose of hydrazine. Apparently the hydrazine did not react immediately with the polymer, resulting in a delayed rise in signal (Ref. 10). Currently, work is continuing on solving this problem, as well as on developing "reversible" polymers where the reaction between hydrazine and the polymer is reversible.

Electronic Nose

An electronic nose is an array of conductometric chemical sensors which change resistance when exposed to vapors. The sensors are not specific to any one vapor; it is the use of an array of sensors, each with a different sensing medium, that gases and gas mixtures can be identified by the pattern of response of the array. A baseline of "healthy air" is established, and deviations from that baseline are recorded as changes in resistance of the sensors. The pattern of distributed response of the sensors may be deconvoluted, and contaminants identified and quantified by using a software analysis program such as pattern recognition and/or neural network (Ref. 11). A miniaturized electronic nose has been constructed at

JPL in collaboration with Caltech. The overall goal of the program is the development of a miniature sensor which may be used to monitor the breathing air in the international space station, and which may be coordinated with the environmental control system to solve air quality problems without crew intervention.

A prototype system will be the subject of an experimental test during a space shuttle flight in late 1998. The sensor head of the Electronic Nose used in this experiment consists of 32 sensor positions arranged on 4 substrates, each with 8 sensor positions (see Figure 4). The polymeric sensor films were made by depositing a solution of polymer mixed with carbon black to make a film 1-5 microns thick in contact with gold electrodes. 16 polymers were used, four on each ceramic substrate. The sensor resistance is sensitive to changes in temperature so the ENose is operated with the sensors held at a constant temperature.

It is apparent that this instrument is very small and lightweight, consisting essentially of nothing but sensor chips, electronics and a small airpump. The system uses a HP200 LX palm top computer and a PIC 16C74A microcontroller. The signals from the various sensors provide a spectrum just like in a mass spec and the computer can match the signals to a standard spectrum for a chemical compound. Although no work has been done on Hydrazine, an organic compound containing nitrogen, indole, was detected at the 30 ppb level. Ammonia and methane were detected at the 20 and 10 ppm level. (Ref. 12). It appears that a search for new polymer/dopant combinations could be made to optimize for Hydrazine detection at ppb levels.

Tunable Diode Laser (TDL) IR Spectrometry

Tunable diode lasers provide a fast and sensitive method for detecting and measuring trace gases in the atmosphere (Ref. 13). A typical configuration is shown in Figure 5. There are two types of lasers which should be considered for this application, namely, the lead salt lasers which operate in the mid-IR, and the short wavelength lasers, based on some combination InGaAsP chemistry, which operate in the near-IR. In order to obtain a sensitive measurement of trace gases it may be necessary to make the measurement over a long path length. Normally the path is folded between two spherical mirrors. The region between the mirrors may be open to the open air or enclosed according to the requirements of the measurement. As many as 100 reflections between the mirrors are easily achieved so that path lengths of 100 m may be obtainable with an overall small package. The power requirements of the TDL are quite modest. The power output of the lasers may be as much as a few mW and no extraordinary precautions need to be taken for eye safety.

Lead salt lasers for mid IR are generally available for operation in the spectral region between about 30 μm and 3 μm . This is the region of strong molecular spectral absorptions. Since the detection method is based on spectral absorptions the lead salts lasers are sensitive detectors of trace gases. The disadvantages of using them comes from the necessity of operating them at liquid nitrogen temperatures. This requires special refrigerants or refrigerators. However, dewars for this purpose are generally available as is liquid nitrogen. The tuning range of these lasers is only of the order of 30-50 cm^{-1} (usually less). This may not be wide enough to be usable for another molecule. So each molecule of interest may require a separate laser. The lasers are quite small (on the order of a mm) and several may be mounted on a cold finger in a dewar.

Short wavelength lasers (near-IR) are constructed using InGaAsP technologies. They produce higher power levels than the lead salt lasers and have the major advantage that they do not require cryogenic temperatures and can operate using thermoelectric coolers. This eliminates the need for special dewars and refrigerants. They have the disadvantage of operating in the short wavelength region(between about 1 and 2 μm) where the absorptions are significantly weaker than at long wavelengths. This is because the molecules absorb in this region in overtones and combinations of their fundamental vibrations; each increasing order of overtone normally carries with it a factor on the order of 100 in diminishing absorption strength. To some extent this loss of sensitivity can be made up by increasing the path length over which the measurement is made.

Previous work on Hydrazine with TDL

Optical techniques are non-intrusive, allowing for accurate on-site measurements without extractive probe systems. Moreover, optical detection in the near infrared spectral region enables the use of communications-grade fiber-optic components and thus offers the opportunity to use multiplexing strategies for making simultaneous measurements of multiple species in multiple locations. A study was made of the 1.55 μm region of hydrazine and MMH, using a commercially available room- temperature diode laser (Ref. 14).

Hydrazine samples were introduced into a quartz cell of 50 cm length and 2.54 cm diameter. Figure 5 shows the experimental schematic of the gas handling and optical measurement system. An external cavity diode laser with a tuning range from 1496.6 to 1582.3 nm was used with two In Ga As detectors for measuring reference and transmitted intensities. The beam path was set up in a three-pass configuration to achieve an effective pathlength of 150 cmAs in previous studies it

was observed that hydrazines decompose when exposed to metal and metal oxide surfaces, permeate through fluorocarbons, and readily adsorb onto most surfaces. It was also found that commercially obtained HZ and MMH contained significant concentrations of dissolved ammonia, presumably due to chemical decomposition. The ammonia was removed by withdrawing the vapor phase above the HZ several times. Absorption survey spectra measurements were made by tuning the diode laser from 6350 cm^{-1} to 6650 cm^{-1} in a single sweep over 3.5 minutes. The peak absorption for HZ and MMH were found to be at 6495 cm^{-1} and 6560 cm^{-1} respectively.

It was concluded that the minimum detectivity was 3 ppm for a 1-meter pathlength. It follows that with a 100 m pathlength we can expect a sensitivity of 30 ppb. A 100 m pathlength is not difficult to achieve. According to Webber et al. (Ref. 14), "the sensitivity of the absorption measurements illustrates the potential for a hydrazine vapor sensor based on near-IR diode-laser absorption spectroscopy". However, "water vapor and ammonia potentially interfere with an optical sensor in this spectral region. A spectrally narrow light source, such as a single-mode diode laser, operating at a carefully chosen wavelength would be suitable for use in an optical probe to avoid these interferences and allow species specific detection."

Quantum-Cascade (QC) Laser Spectrometer

A huge leap in laser technology has been made in the last year or so that has produced room-temperature tunable laser sources in the mid-IR from a revolutionary new approach to laser fabrication, that of quantum engineering of electronic energy levels to produce Quantum-cascade (QC) lasers in the $3\text{--}12\text{ }\mu\text{m}$ range. These new devices produce single-mode laserlight tunable over $10\text{--}20\text{ cm}^{-1}$ with output power of fractions of a watt, hundreds of times greater than that of lead-salt lasers at cryogenic temperatures. Furthermore, these devices are highly reliable, with long-duration spectral integrity. The technological breakthrough provided by the invention of the QC laser offers a ten-fold increase in the current ability to address the HZ minimum detection limit. Progress in QC laser development has been very rapid. Room temperature (300 K) operation has been demonstrated in pulsed operation from 5.2 to $8.2\text{ }\mu\text{m}$, with extremely high output peak powers of 200-520 mW (Ref.'s 15, 16).

It is apparent that the substitution of QC lasers for the lead-salt lasers described above will eliminate the requirement for liquid nitrogen to cool the sensors, while at the same time increasing the sensitivity. The question is when these units will be available commercially.

TDL SPECTROMETER DEMONSTRATION WORK AT JPL

This work was carried out by Christopher R. Webster, Randy D. May, Jack S. Margolis, and Mark S. Anderson.

Starting out in 1981 with helium-cooled laser instruments onboard balloons, the JPL technology has developed into a liquid nitrogen-cooled 50 m optical path instrument of 55 lbs (ALIAS II) onboard an aircraft in 1993. A room temperature diode laser instrument was developed in 1994 with an optical path of 50 m and an instrument weight of 7 lbs. Recently, a miniature near-IR diode laser sensor for Mars atmospheric studies, with a mass of the order of one lb., was delivered for the Mars 98 MVACS payload.

Experimental Work

It was decided to demonstrate the technical feasibility of the TDL IR Spectrometer for measuring Hydrazine at the 10 ppb level, using the existing ALIAS instrument. (Ref. 17) The Aircraft Laser Infrared Absorption Spectrometer (ALIAS) instrument is a 4-channel scanning tunable diode laser spectrometer that uses high-resolution laser absorption in the $3\text{--}8\text{ }\mu\text{m}$ wavelength region to directly and simultaneously measure any four of the gases HCl, NO_2 , CH_4 , CO, and N_2O . Both direct absorption and second-harmonic detection techniques are used to measure the fractional absorption from individual or groups of single vibrational lines for each gas, with line-center absorptions typically a few percent for the tracers N_2O , CH_4 , and CO, and less than 0.05% for HCl and NO_2 . The instrument samples the atmosphere using a fast flow system with a flow rate of 16 liters/sec at 65 mbar driven by inlet ram pressure and by aerodynamic vacuum at the exhaust. The flow system is in two parts, a heated inlet with wall temperatures of $60\text{--}70^\circ\text{C}$, and a multipass optical (Herriott) cell. All interior surfaces are coated with a halocarbon wax from a chloroform solution to minimize wall loss. Extensive calibration and testing of the inlet and sampling system, including post-flight ion-analysis of the inlet residue, has revealed no systematic instrument or sampling error that could result in measured gas loss of greater than 10%. calibration gas standards are used.

The Hydrazine Spectra

N_2H_4 has a strong absorption band in the mid-IR near $10.6\text{ }\mu\text{m}$ (see Figure 6), and a weaker band towards the near-IR region of $2.985\text{ }\mu\text{m}$. The upper panel of Figure 12 shows the FTIR high resolution (0.125 cm^{-1}) spectrum recorded from 740 to 1050 cm^{-1} at 400 ppm-meters in 1 atm. nitrogen (Infrared Analysis, Inc.). The middle panel is an expansion in

wavenumbers of the region from 930 to 980 cm^{-1} , for comparison with the synthetic spectrum of NH_3 in this same region (lower panel), degraded to a resolution similar to that of the FTIR.

For spectroscopic detection of N_2H_4 using the 10.6 μm -band, spectral regions including strong NH_3 lines (features) or CO_2 lines must be avoided. We identify the strong hydrazine absorption features at 940 cm^{-1} -showing minimal contribution from NH_3 interferences- were identified as suitable candidates for hydrazine gas detection. The synthetic second harmonic spectrum in this region is shown in Figure 7. For the studies reported here, our particular laser diode could not scan over these preferred lines, and we could only study the narrow regions near 962 cm^{-1} and 965 cm^{-1} where strong NH_3 interferences were expected. However, the much higher resolution (0.001 cm^{-1}) of the TDL spectrometer compared with the FTIR spectrometer means allowed individual lines (features) of N_2H_4 to be identified away from interferences from either NH_3 or CO_2 , especially at lower pressures (Ref. 18).

Figure 8 shows TDL spectra of N_2H_4 recorded by ALIAS using an evacuated Herriott cell injected with pure N_2H_4 and back-filled with dry nitrogen to the pressures indicated. The wavenumber scale was calibrated using a monochromator in combination with recorded spectra (Fig.9) of NH_3 , N_2O , and CO_2 . Strong NH_3 lines at 965.354 cm^{-1} and 962.17 cm^{-1} are identifiable in the spectrum, and are used to monitor the NH_3 impurity, and its production from N_2H_4 degradation.

For the 962 - 965 cm^{-1} region scanned by this laser, we identified a N_2H_4 line (feature) at 961.75 cm^{-1} free from NH_3 absorption which would be suitable to monitor hydrazine levels. In the lower three panels of Figure 8, second-harmonic (2f) spectra of this region show the degradation of detectivity of N_2H_4 with increasing pressure. This degradation has two components: first, the combination of pressure-broadening and higher laser modulation levels produces a second harmonic spectrum which is dominated by isolated NH_3 lines; second, at the N_2H_4 concentrations used, increasing buffer gas (N_2) pressure serves to dissociate hydrazine into ammonia, as can be seen by comparing the relative sizes of the features at 961.75 cm^{-1} and 962.17 cm^{-1} .

With relatively high concentrations (> few ppm) of N_2H_4 in the cell in 10 mbar or more N_2 gas pressure, we could watch the continuous growth of NH_3 lines relative to those of N_2H_4 with an e-folding time of about 5 minutes. However, we caution that in this observation we could not unambiguously identify that the production of ammonia was from hydrazine dissociation and not simply outgassing from the cell walls, since NH_3 is notorious for sticking to walls. (N_2H_4 is also expected to stick to walls).

Sensitivity Study

Minimum detectable mixing ratios of N_2H_4 were estimated by measuring the signal-to-background ratios obtained for actual hydrazine spectra (direct, second-harmonic, and empty cell), which were then related to the concentrations used in the FTIR study of Anderson (JPL in-house work). From the FTIR study, strong features in the 10.6- μm band have absorbances of about 0.12 for a 400 ppmv-meter sample, and those at 2.98 μm have absorbances of about 0.016 for the same conditions. We therefore determine that the stronger features near 940 cm^{-1} correspond to absorption levels of about 0.01 % for 1.5 ppbv N_2H_4 in the 80 m pathlength of ALIAS. The minimum detectable absorptions measured in our laboratory experiments reported here correspond to detection limits of about 1 ppb for N_2H_4 in a reduced pressure (0.1 atm) cell, or about 50 ppb N_2H_4 in a 1 atm. environment.

LAB MEASUREMENTS WITH 80-M PATHLENGTH:

Total Pressure	Minimum detectable absorption	Minimum detectable mixing ratio N_2H_4 at 962 cm^{-1}	Minimum detectable mixing ratio N_2H_4 at 940 cm^{-1}	Measurement time
100 mbar	0.005 %	2.4 ppb	0.8 ppb	3 sec
1 atm.	0.1 %	50 ppb	17 ppb	3 sec

PROPOSED INSTRUMENT CONCEPT AND SENSITIVITY

In order to relax requirements on weight, optical stability, size, and pumped volume, we propose a TDL spectrometer for N_2H_4 measurement which is based on a modest 20-meter pathlength. We present three basic options: one sampling at reduced pressure (100 mbar) and operating at 940 cm^{-1} based on a liquid-nitrogen-cooled TDL at $10.6\text{ }\mu\text{m}$ with high-sensitivity (5 ppb); a second sampling at ambient pressure (1 atm) with an open-path cell capable of detecting down to 70 ppbv, with similar characteristics to the first system; and a third option using reduced pressure (100 mbar) sampling, but operating at 3350 cm^{-1} based on room-temperature TDL at $2.9\text{ }\mu\text{m}$ with reduced sensitivity (40 ppb).

OPTION 1: Reduced-pressure high-sensitivity detection (5 ppb)

- high-sensitivity detection to 5 ppb N_2H_4
- lead-salt TDL at 940 cm^{-1}
- liquid nitrogen cooled dewar
- 20-meter total path
- reduced pressure (0.1 atm) sample cell
- small-volume (1 liter) cell with heated outgass option
- instrument weight about 20 lbs
- PC graphics/data storage/records

OPTION 2: Ambient pressure detection (70 ppb)

- detection to 70 ppb
- lead-salt TDL at 940 cm^{-1}
- liquid nitrogen cooled dewar
- 20-meter total path
- atmospheric pressure (1 atm) open-path cell
- instrument weight about 20 lbs
- PC graphics/data storage/records

OPTION 3: Reduced-pressure low-maintenance detection (40 ppb)

- sensitive detection to 40 ppb
- room-temperature TDL at 3350 cm^{-1}
- no cryogenics needed
- 20-meter total path
- reduced pressure (0.1 atm) sample cell
- small-volume (1 liter) cell with heated outgass option
- instrument weight about 5-10 lbs
- PC graphics/data storage/records

Note that these studies were made on pure N_2H_4 injected into dry N_2 gas at pressure. It is known that even in moderate concentrations N_2H_4 reacts with air to produce NH_3 as final decomposition product. It is questionable whether N_2H_4 can maintain high levels in the CO_2 and H_2O environment of ambient air, and it is suggested that NH_3 may prove a good alarm for N_2H_4 presence. This latter idea could be pursued in subsequent field release tests, but it is attractive because of the higher sensitivities achievable with NH_3 detection.

CONCEPTUAL DESIGN CONSIDERATIONS

One can envision an application where the optical path is the room or highbay itself, i.e. an open optical path where the TDL is located on one wall and the sensor is located on a wall 20 meters away so no mirrors are needed. This represents a sensitivity of 70 ppbv. Now if two mirrors are mounted on opposite walls and the optical path is increased by reflecting the laser beam 8 times, the optical path is 160 meters and the sensitivity would be 8 times better or $70\text{ppbv}/8$ is 9 ppbv. In practice one would use a retroreflector on one wall and a mirror incorporating the laser outlet and the sensor inlet on the other wall. This case is shown as Option 4 in the table below:

Various Design Concepts

CASE NO.	SENSI-TIVITY ppb	OPTICAL PATH m	NO. of REFLEC-TIONS	TUBE LENGTH cm	LN2	ATM	LBS
1	5	20	40	50	YES	0.1	20
2	70	20	40	50	YES	1.0	20
3	40	20	40	50	NO	0.1	5-10
4	9	160	8	2000 (room)	YES	1.0	20
5	20	40	80	50	NO	0.1	5-10
6	20(HZ) 2(NH3)	40	80	50	NO	0.1	5-10
7	1	40	80	50	NO	0.1	5

An example of a TDL IR Spectrometer is shown in Figure 9, showing laser beams traversing the sample space between the two mirrors. The electronics package is shown in the background.

New strategy using Ammonia as a Tracer

As mentioned above, ammonia was always present when the hydrazine concentration was measured. It was observed that the ammonia signal was at least an order of magnitude stronger than the hydrazine signal. Hydrazine is the source of the ammonia, as hydrazine quickly decomposes into ammonia. The suggestion was made that using ammonia as a warning signal could be a valid strategy. In fact, because ammonia is easier to detect and gives a stronger signal than hydrazine, it might be easier to detect ammonia at the 1ppbv level than hydrazine at the 10ppb level. This suggests using two TDL sensors, one for ammonia and one for hydrazine.

It is easy to put 2 TDL's in one instrument as they are so small in size (one quarter inch). In fact, the ALIAS instrument has 4 TDL's with one set of mirrors in one tube. It should also be noted that independent TLD's for MMH and UDMH could be added to the instrument if necessary. It may be suggested that there could be other sources of ammonia present such as Windex, etc. It should also be noted that most fueling bays are well ventilated and no other ammonia sources are therefore likely to be present. The probable absence of other ammonia sources can be established by taking readings on the site before hydrazine operations start.

Another case is thus proposed, namely one with two TLD sensors, one for ammonia and one for hydrazine. This case could be an extension of case 5 by adding the ammonia sensor. This case is shown as option 6 in the table above.

Future use of the Quantum- Cascade Laser

As described earlier, the recent development of the QC laser has increased the sensitivity of the TDL Spectrometer at least an order of magnitude. Also there is no need for any cooling, as the units operate very well at room temperature. There will probably some time period before the QC lasers will be available. This suggests that Option 6 in the previous Section can later be retrofitted with the QC laser when it becomes available. The retrofitted Option 6 is shown as Option 7 in the table above.

CONCLUSIONS

1. There are three measurement concepts that have the potential to meet the requirements of 10ppb, fast response, low maintenance, portability, and reasonable cost. They are the TDL IR Spectrometer, the electronic nose, and the ion mobility spectrometer.
2. Based on this study, the fast-response detection of hydrazine and its derivatives at the sub-ppb-level sensitivity will best be achieved using the direct, non-invasive optical technique based on tunable laser spectroscopy. A miniature room-temperature laser spectrometer using either near-IR or Quantum-Cascade lasers would be able to meet the sensitivity requirements while still offering high specificity through unambiguous spectral recognition. The technique has a strong heritage of demonstrated sensitivity through aircraft, balloon, planetary spacecraft, space station, and industrial applications such as automotive and fabrication monitoring. Based on existing near-IR instruments weighing under 20 lbs., it is reasonable to assume that a room-temperature laser sensor can be built specifically for hydrazine and derivatives that is simple, reliable, and of low-maintenance. A two-channel laser spectrometer measuring both hydrazine and ammonia simultaneously is recommended.

The current laboratory work demonstrated the 10 ppb sensitivity in an earth application with lead salt lasers and LN2 cooling. The use of near-IR lasers will eliminate the LN2 cooling requirement, but reduces the sensitivity to 20 ppb. However, this can be compensated for by adding an ammonia laser sensor with a 2ppb sensitivity that acts as a warning below the 20ppb level of the hydrazine detector. The use of the new QC laser will increase the sensitivity of this instrument by an order of magnitude. No special cooling is required and the ammonia sensor is not needed. A QC laser instrument will meet all requirements.

3. The ion mobility spectrometer has a military background in nerve gas detection at low levels and more recent applications in detecting contaminants in refinery gas streams. Previous hydrazine tests failed to meet various requirements but the technology has the strongest potential for very low sensitivity of all systems considered. Testing the latest technology in this area is needed.

4. The electronic nose concept has been demonstrated at the sub ppm sensitivity level for an amine compound. There is great potential for a simple, extremely lightweight, portable, cheap instrument. Some development work is needed.

5. Work under way in miniature GC and miniature Mass Spectroscopy instruments has definite future potential to meet the hydrazine detection requirements.

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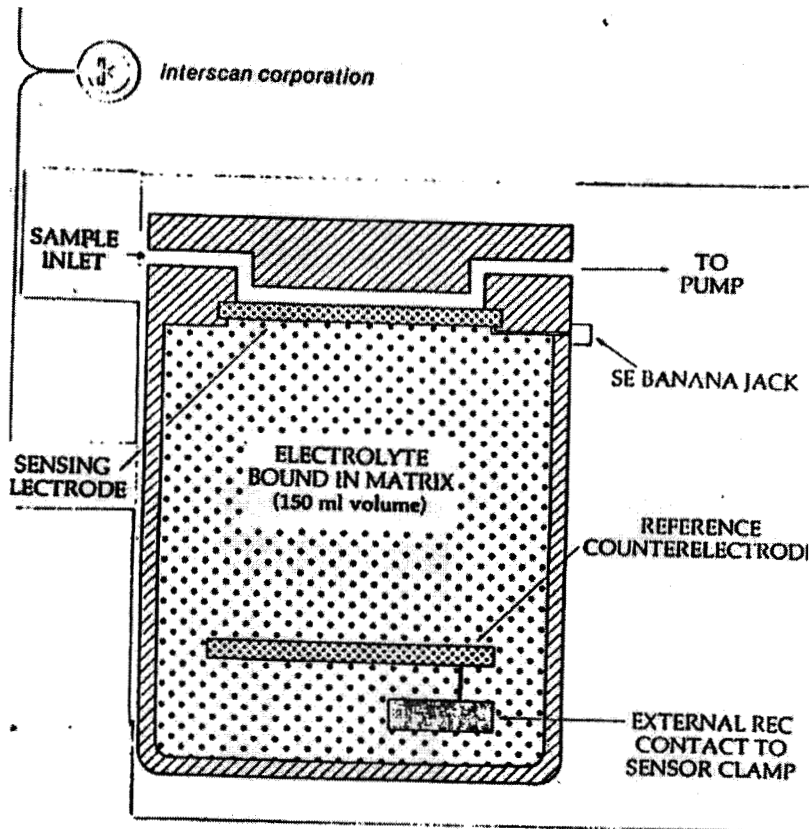


Figure 1 Interscan Sensor (Diagrammatic Illustration).

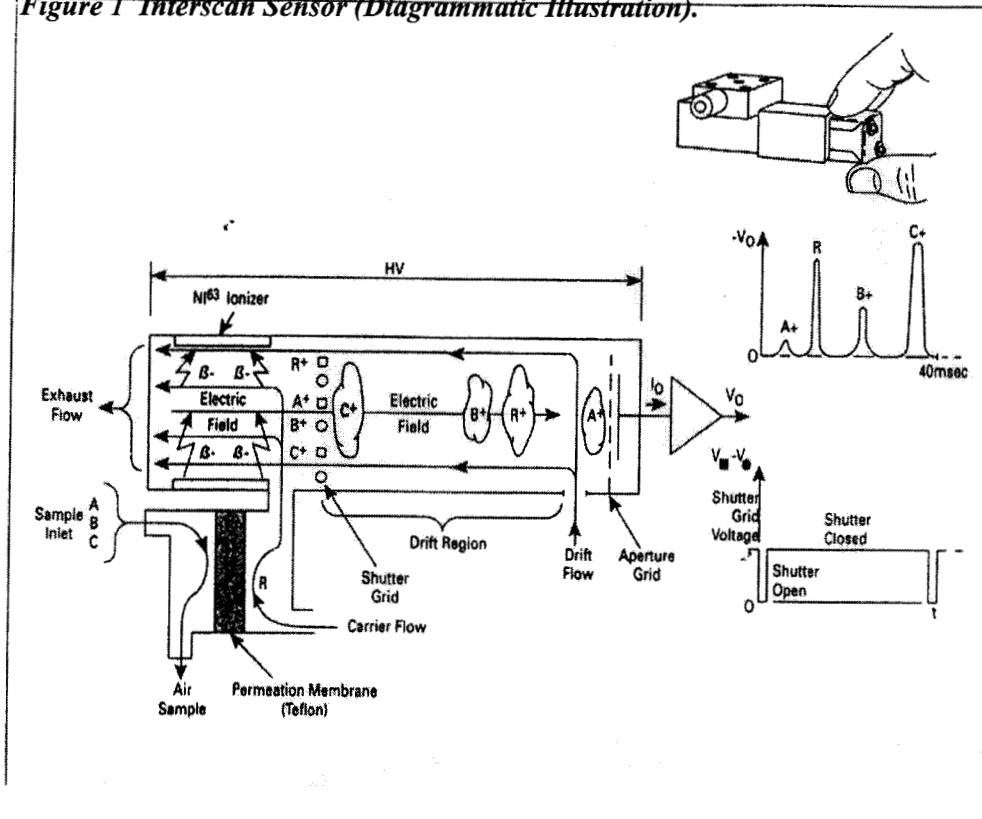


Figure 2. Schematic of an IMS Cell.

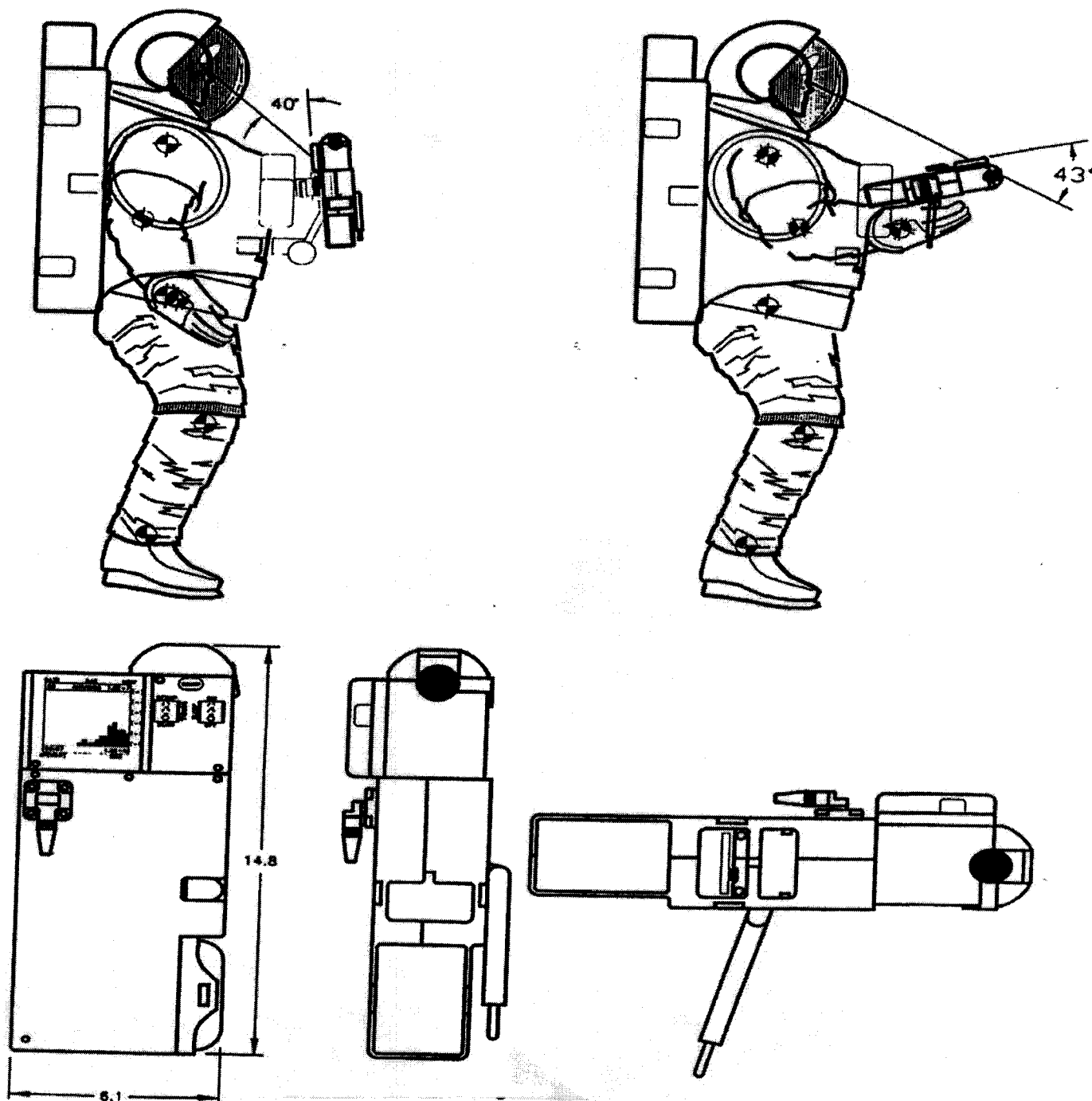


Figure 3. TGA with PGT Eva Battery Pack and Fixed Display.

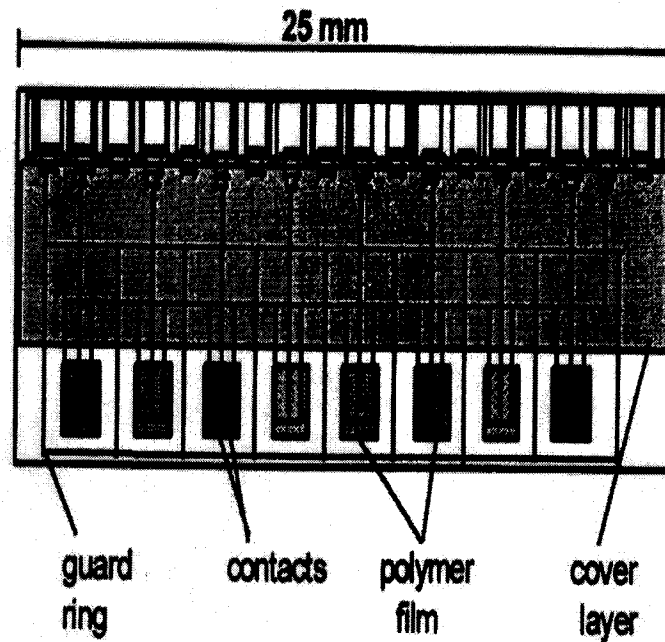


Figure 4 *Sketch of the Ceramic Substrate Chip Containing Eight Sensors*

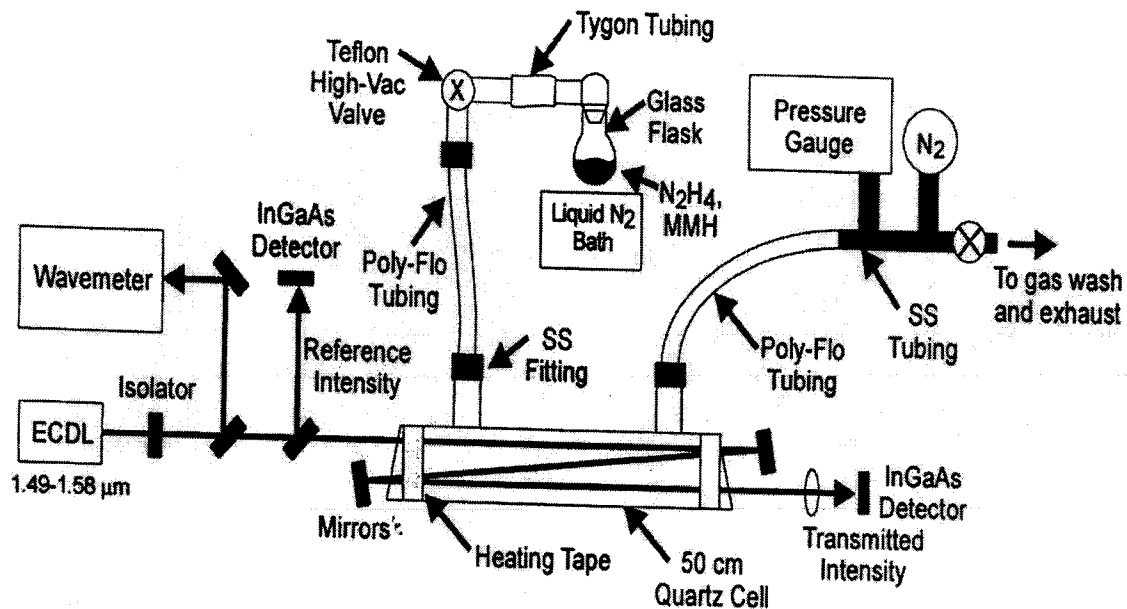


Figure 5. *Experimental Schematic of the Gas Handling and Optical Measurement System of a TDL System*

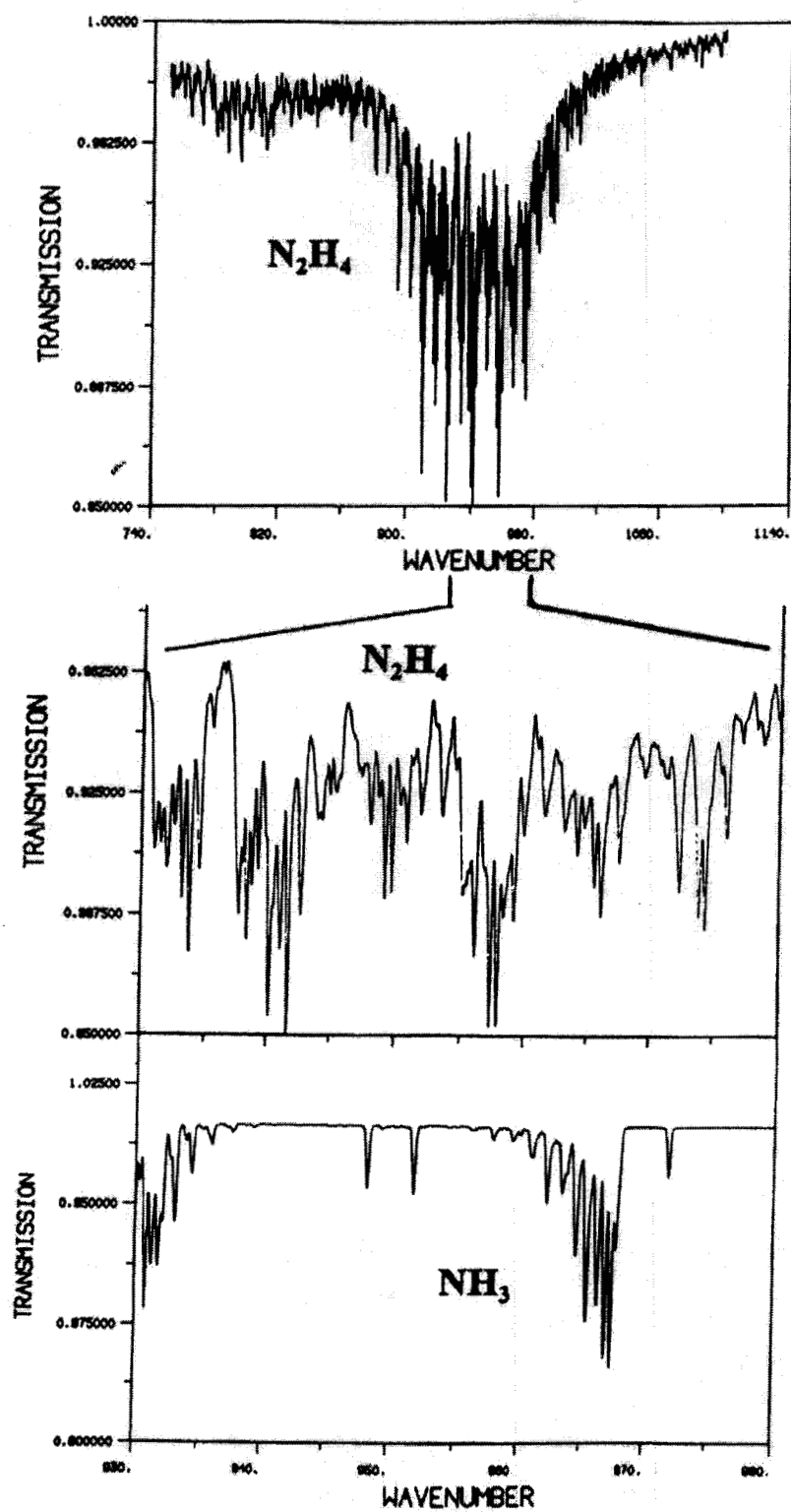


Figure 6. Hydrazine Spectra.

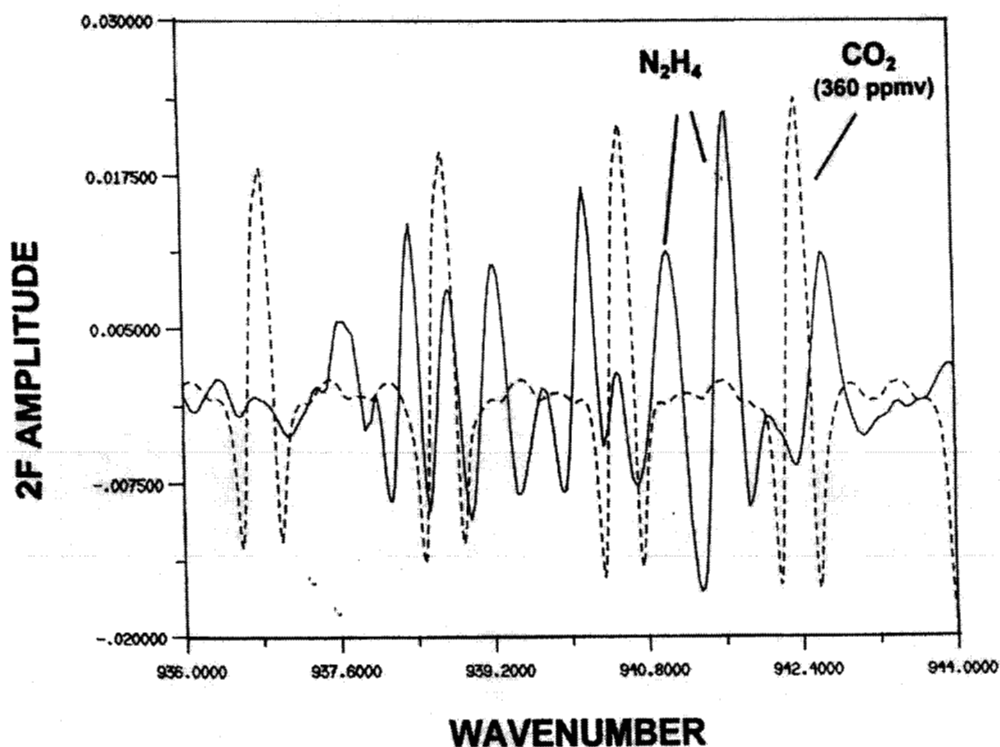


Figure 7 Second Harmonic Spectrum

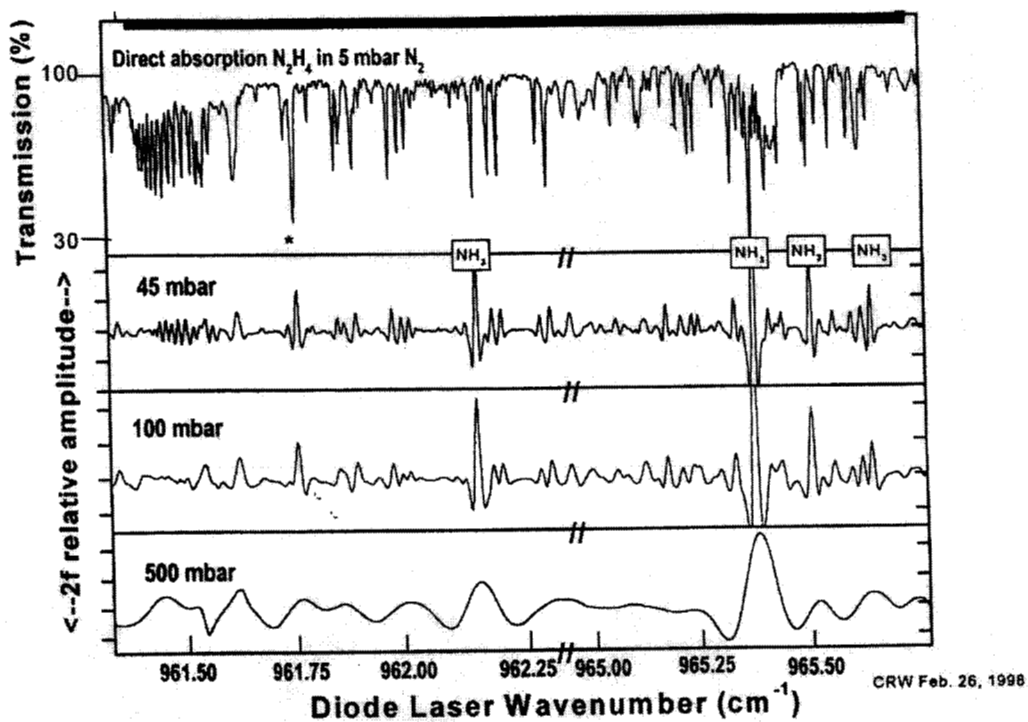
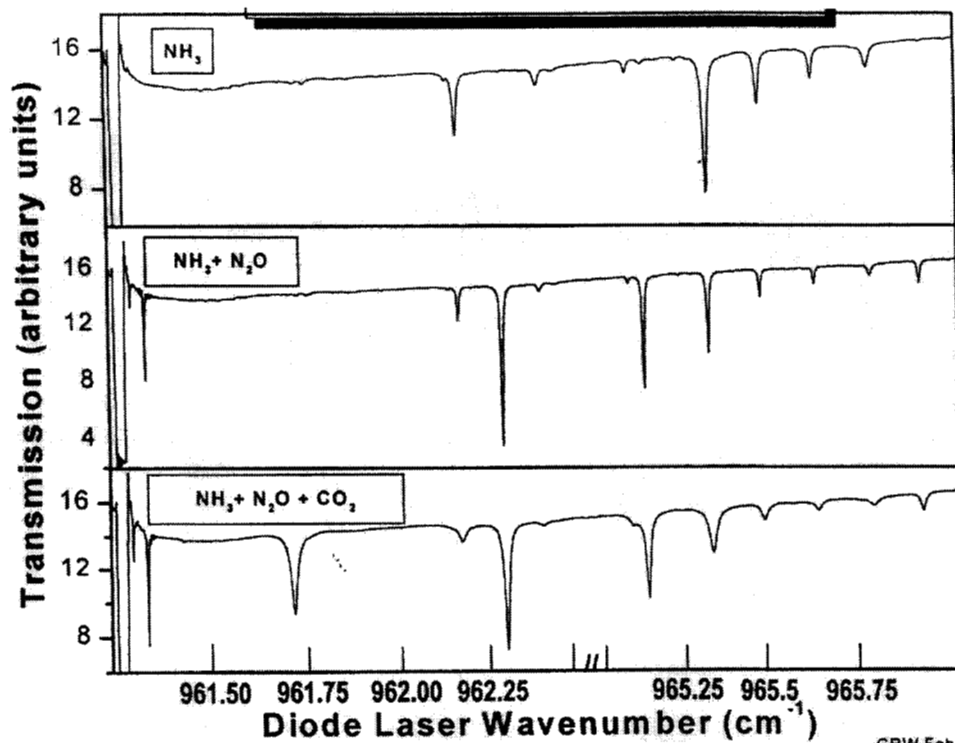


Figure 8. TDL Spectra of Hydrazine (N_2H_4) and Ammonia (NH_3)



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Figure 9. Recorded Spectra of NH_3 , N_2H_4 , N_2O and CO_2

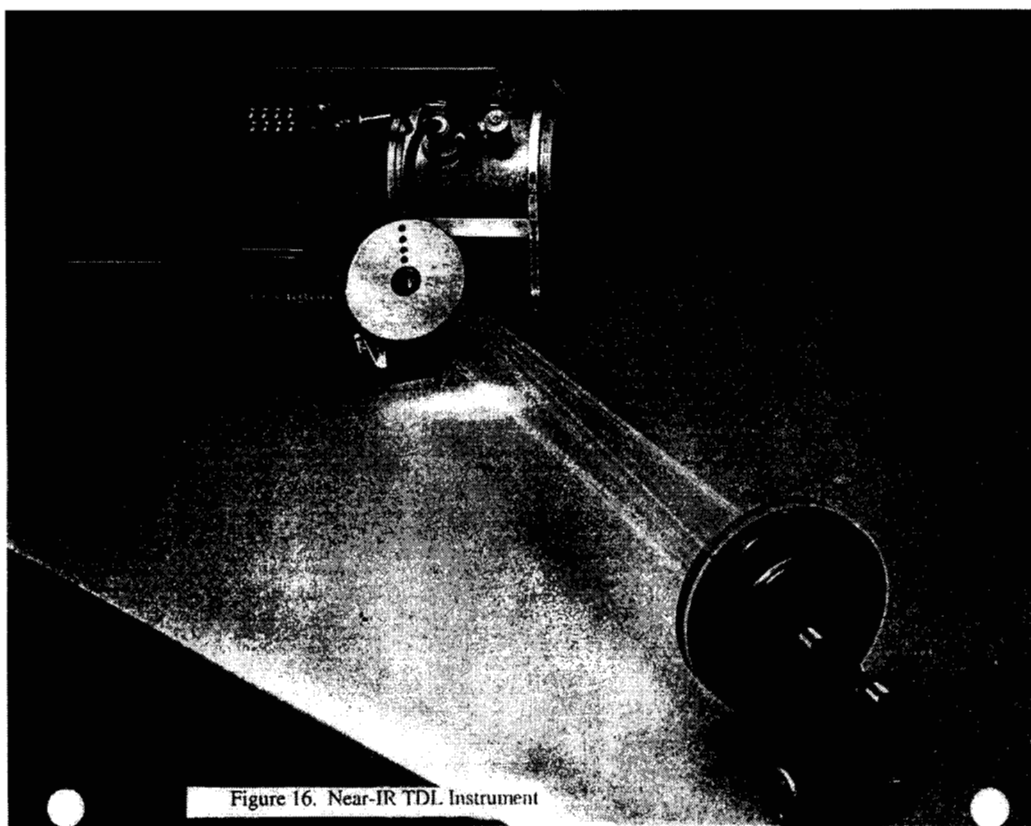


Figure 10 TDL IR Spectrometer